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The Paleozoic Sedimentary Rocks of the Ouachita Mountains and their Genetic Relationship to
the Mississippi Valley-Type Mineralization in the Southern Ozark Region:
Insights from Radiogenic Pb Isotopes and Trace Elements Studies

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Geology

by

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August 2019
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Abstract

Cluster of Pb and/or Zn deposits of the well-known Tri-State and Northern Arkansas Mississippi Valley Type (MVT) districts located north of the Arkoma basin and the Ouachita fold-thrust belt in north America are genetically connected to the Pennsylvanian-Permian Ouachita orogeny which triggered a South-North topographic gradient flow of basinal brines, leaching metal rich sediments en route. The objective of the research is twofold. First, to ascertain whether the organic-rich shales and sandstones from the study area provided metals during the mineralization event, which was coeval with the Ouachita orogeny. Second, to assess the depositional environment of the potential source rocks, which will shed light on their ability to sequester metals. The Pb isotope compositions of the ores (sphalerite) have been compared to their associated sedimentary rocks (Collier, Mazarn, and Polk Creek, Womble, Fayetteville, Stanley and Chattanooga shales and Jackfork Sandstone) and metal sources have been evaluated. In addition, the role of depositional redox of sedimentary rocks to sequester adequate amounts of metals has been appraised using redox sensitive trace elements (U, V, Mo, Cr, etc.). The Pb isotope compositions of the ores (sphalerite) have been compared to those of the sedimentary rocks of the Ouachita Mountains (Cambrian Collier Shale, Early Ordovician Mazarn Shale, Middle Ordovician Womble Shale, Late Ordovician Polk Creek Shale, Mississippian Stanley Shale, and Pennsylvanian Jackfork Sandstone) and the Ozark Plateau (Devonian/Mississippian Chattanooga Shale and Mississippian Fayetteville Shale). Metal sources evaluation indicate a mixing model of fluids sourced from high and less radiogenic rocks shown by a broad and linear trend of Pb isotope composition, with the Chattanooga rock and the Jackfork sandstone samples being the most prominent source rocks. Paleoredox proxies indicate deposition under anoxic and Euxinic condi-

tions, which are favorable for metal enrichment. However, oxic-suboxic conditions are also indicated by other geochemical proxies, suggesting the possible first order control of primary production that has resulted in increased flux of organic matter. Additional factors such as the basin geometry, the rates of sediment accumulation, the post depositional alteration processes associated with diagenesis and low-grade metamorphism during the Ouachita orogeny might have overprinted the depositional signatures.

Acknowledgements

I would like to thank all the people and institutions that, in many and at different stages, have contributed to the success of this work.

Foremost, I would like to express my gratitude to the Fulbright program for the financial resources without which this work would not have been possible. Many thanks to my thesis advisor, Dr. Adriana Potra, whose patience, motivation, and knowledge invaluabley contributed to this research. Her relentless assistance, compassion, and unique character make her a good advisor. My great appreciation to my thesis committee members, Dr. Philip Hays and Dr. Thomas McGilvery, for their insightful comments.

My special thanks are extended to the University of Arkansas, especially the faculty and staff of the Department of Geosciences, for their support throughout the program. For the very rare, but valuable meetings, my heartfelt gratitude goes to Dr. Lamb and Dr. Holland. To my friends, classmates and officemates, I appreciate your support and the atmosphere of fun and good vibes that you created.

Table of Contents

1. Introduction.....	1
2. Geological setting	4
3. The Tri-State and Northern Arkansas Mississippi Valley-type Districts	8
4. Sampling and Analytical Methods.....	14
<i>4.1 Sample Processing</i>	<i>14</i>
<i>4.2 Chemical dissolution and analyses of whole-rock samples for Pb isotope composition</i>	<i>15</i>
<i>4.3 Chemical dissolution and analyses of leachates for Pb isotope composition.....</i>	<i>17</i>
<i>4.4 Chemical dissolution and analyses of whole-rock samples for trace element concentration</i>	<i>18</i>
5. Metallogenetic study.....	20
6. Paleoredox and paleoproductivity investigations of the Study area	31
7. Conclusions and future directions.....	45
Reference	47

List of Figures

- Figure 1.** (a) Geologic sketch map showing the location of major MVT ore districts of the Ozark region (b) Cross section showing brine migration (in arrows) during MVT mineralization event (Modified from Lopaka L.,2000). 111
- Figure 2.** Location of rock samples in the Ouachita Mountains and the Ozark region (the Fayetteville and the Chattanooga shale sample data were taken from Bottoms et al.,2019).**Error! Bookmark not defined.**
- Figure 3.** Stratigraphic position of the rock samples in the stratigraphic section of the Ozarks and Ouachitas. Figure 2 gives the location of each rock sample (Retrieved from <http://www.geology.ar.gov/geology/stratigraphy.htm>). 133
- Figure 4.** Thorogenic (a) and Uranogenic (b) diagrams depicting the Pb isotope compositions of ores from the Northern Arkansas and the Tri-State MVT districts, and the whole rock samples of the study area. The orogene (OR) and upper crust (UC) growth curves are from Zartman and Doe (1981). 266
- Figure 5.** Thorogenic (a) and Uranogenic (b) diagrams depicting the Pb isotope compositions of ores from the Northern Arkansas and the Tri-State MVT districts, along with the age-corrected (250 Ma) Pb isotope values of whole rock samples of the study area. 288
- Figure 6.** Thorogenic (a) and Uranogenic (b) diagrams showing the Pb isotope compositions of ores from the Northern Arkansas and the Tri-State MVT districts, along with the measured Pb isotope ratios of the leachates. 300
- Figure 7.** Redox classification of depositional environment (adapted from Tyson and Pearson,1991). 322
- Figure 8.** Vertical profiles of electron acceptors in marine sediments (Adapted from Kristensen, 2000). 333
- Figure 9.** Correlations of various redox-sensitive TEs with the detrital TE Ti. The lower the coefficient of determination (R^2) between a TE and Ti, the higher its authigenic input. In decreasing order of authigenic input, the TE are Th, U, Cd, Mo, Zn, Cu, Pb, V, Cr, Co, and Ni. 400
- Figure 10.** Constraints on the paleoredox conditions during deposition of the rock samples from the Ouachita Mountains and the Arkoma Basin based on Ni, Cu, Mo, U and V behavior (adapted from Tribovillard et al., 2006). 411
- Figure 11.** Reconstruction of the paleoredox conditions during deposition of the sedimentary rock samples in the study area using the $V/(V+Ni)$ ratio. According to this geochemical proxy, most of the rock samples were deposited during anoxic conditions. 433

List of Tables

Table 1. Description of rock samples of the study area. Geographic locations of the rocks are provided in Table 2.....	7
Table 2. Measured Pb isotope composition of the whole rock samples from the Ouachita Mountains and Arkoma Basin	25
Table 3. Age-corrected (250 Ma) Pb isotope composition of the whole rock samples from the Ouachita Mountains and Arkoma Basin.....	27
Table 4. Measured Pb isotope composition of the leachate fraction of rock samples from the Ouachita Mountains and Arkoma Basin.....	29
Table 5. Concentration in ppm of Trace Elements and the value of the paleoredox proxy $V/(V+Ni)$	36
Table 6. Values of the Enrichment Factor of Trace Elements used for the paleoredox and paleoproductivity study.	37

1. Introduction

Mississippi Valley Type (MVT) deposits are sedimentary rock-hosted hydrothermal lead-zinc (Pb-Zn) systems characterized by (1) low-temperature formation of circa 50° to 200°C, (2) epigenetic mineralization hosted within unmetamorphosed platform carbonate sequences, usually in cluster and located adjacent to sedimentary basins or foreland thrust belts, (3) precipitation from highly saline brines of 10 to 30 wt. % salts, (4) sphalerite and galena are the dominant ores with minor amounts of iron sulfides and the presence of carbonate, barite and/or fluorite as gangue minerals, and (5) sedimentary sources of metals and sulfur, except the Kentucky-Illinois fluorite district assumed to be associated to igneous activity (Ohle, 1959; Anderson and MacQueen, 1982; Sangster, 1983; Leach and Sangster, 1993; Sangster, 1995; Misra, 1999; Leach et al., 2001). MVT deposits are distributed in space corresponding to passive margin settings or rifts and inherently associated with the evolution of sedimentary basins. The sedimentary basins host mineral and energy resources, mainly lead (Pb) and zinc (Zn) ores, oil and gas, thus implying a possible interaction during migration of hydrocarbons and ore fluids (McCuaig et al., 2018). The distribution of MVT deposits has a time constraint as well, mostly linked to the first Great Oxidation Event and the onset of an oxidized shallow hydrosphere (Leach et al., 2010; Groves et al., 2005). Conundrum on the ambivalence character of the MVT deposits is still unsettled; Being amongst the simplest metalliferous ore deposits by their mineralogy, low pressure and temperature formations and ubiquity in an undeformed and unmetamorphosed platform carbonate rocks, MVTs are also complex by their connection to the evolution of sedimentary basin, a long temporal and spatial process (Anderson, 1978). In addition, based on the LA-ICP-MS analysis of the mineralizing brines of the Northern Arkansas and Tri-State MVT districts, Stoffell et al. (2008) found anomalous metal-rich fluids associated to mineralization, explaining that they are not only

the result of typical basin evolution considering that some forelands are mineralized while others are barren. Extending this complexity to mineral and petroleum systems in sedimentary basins, to fill out the knowledge gap for an accurate targeting of mineralized foreland basin, McCuaig et al. (2018) suggested reconstruction of paleotectonic, paleogeographic and paleoenvironment factors as critical in basin selection.

Accounting for 24 % of the worldwide Pb and Zn resources, the MVT Pb-Zn deposits comprise the largest recognized concentration of Pb in North America in the Ozark region. Scattering MVT districts in North America encompass, among others, the well-known Tri-State (Oklahoma-Kansas-Missouri), Central Missouri, Southeast Missouri (the Old Lead Belt and the Viburnum Trend) and Northern Arkansas districts (Fig. 1), located north of the Arkoma basin and the Ouachita fold-thrust belt (Leach and Taylor, 2010).

If genetic factors associated to the source(s) of the metals in the Ozark MVT deposits is still heavily debated, the constraint on paleoredox and paleoproductivity of the depositional environment of metal-rich rocks alleged to have provided Pb and or Zn to the ore fluids is limited or nonexistent. Studies carried out in the Ozark MVT districts have agreed on the genetic association between the mineralization and the south-north migration of basinal brines triggered by the Ouachita tectonic events (Leach, 1994). However, debate abounds in terms of the source(s) of metals. Some authors claim that the Pb and/or Zn mineral bodies in the Ozarks are the products of mixing of metals from various sources (the mixing model), including a large input of metals from the basement rocks (Goldhaber et al., 1995; Leach et al., 2010). Other authors argue in favor of metal contribution from organic-rich shales: Schutter (2015) correlates the mineralization exclusively to the proximal metal-rich organic shales, while Crocetti et al. (1988) suggest input

of metals from both, the basement rocks and the proximal shales. Bottoms et al. (2019) favor input of Pb mainly from organic-rich shales; however, the authors do not exclude the possibility of some Pb being supplied by the basement rocks.

The main objective of this study is to shed light on the relationship between the metal-rich shales in the Ouachita Mountains and the Zn-Pb ores from the Northern Arkansas and the Tri-State MVT mining districts. This is carried out by comparing the Pb isotope compositions of ores from both districts to the Pb isotope compositions of whole-rock sedimentary rocks, represented mainly by shales and minor sandstones, of the Ouachita Mountains. Leaching experiments on whole-rocks from the Ouachita Mountains and the Ozark Plateau are performed to determine the ability of the hydrothermal fluids to leach metals from the whole-rocks. Published Pb isotope data of MVT ores from the aforementioned MVT districts (Potra et al., 2018; Bottoms et al., 2019) and of sedimentary rocks from the Ozark Plateau (Bottoms et al., 2019) are incorporated for a systematic and comprehensive approach of the investigation. The advantages of using Pb isotopes over other radiogenic tracers are twofold. First, the fact that different parent isotopes, namely uranium (U) and thorium (Th), disintegrate into two different Pb daughter products offers the possibility for Pb isotopes to be used for studying a wide range of geological processes. Additionally, in aqueous environments and oxidizing fluid systems, the parent elements U and Th have contrasting geochemical behavior. The U ions turn into uranyl ions, which are easily mobilized and fractionated from Th. However, due to their high atomic weight, Pb isotopes are stable and do not fractionate under different physical and chemical conditions (Gulson, 1986). Redox sensitive trace elements will shed light on the fertility of source rocks via the characterization of the redox conditions in the past marine depositional setting of sedimentary rocks of the study area.

In addition to being classic, the Northern Arkansas and the Tri-State regions have been the center of attention to many geologists, prompting intense investigations. Thus, the area provides a profusion of geological and geochemical data, which present a solid scheme of comprehension from which the results of this study will benefit.

2. Geological setting

Rock samples in the study area consist of Paleozoic sedimentary rocks, ranging southward from the shallow water facies to clastics to deep water facies. Rock descriptions will be restricted to only those that were sampled in the study area (Table 1). Thick sequences of carbonate rocks comprise the major rock facies in the Ozark Plateau, with the Springfield Plateau aquifer being the host package for the Tri-State mineralization; the ores are mainly located in the Mississippian cherty limestones of the Warsaw and the Keokuk Formations. The lithostratigraphic succession in the Ozark region (Fig. 2) consists of, in ascending order, Precambrian igneous and metamorphic rocks capped with dolomite, limestone, and shale of Cambrian to Pennsylvanian age (McKnight and Fisher, 1970). The Chattanooga Shale (Devonian-Mississippian) was deposited in anoxic environments during the Kaskaskian marine transgression and covers a large portion of North America. The lower, middle and upper members of the Chattanooga Shale correspond to the transgressive, early highstand, and late highstand depositional systems, respectively. The middle shale member of the Chattanooga is regarded as the thermally mature petroleum source rock, with the highest radioactivity of all three members (Lambert, 1993). The Fayetteville Shale (Late Mississippian) is black marine shale, deposited on a southward deepening ramp in northern Arkansas. Interbedded limestones, increasing upward in volume and size throughout the shale sequence, are attributed to increasing energy environments and shallowing-upward history. The upper and lower members are the major facies comprising the Fayetteville

Shale (Handford, 1986). The lower stratigraphic section is an organic-rich facies consisting of black, pyritic shales with intercalations of siliceous chert and siltstone (Ratchford and Bridges, 2006). The upper Fayetteville Shale is a transitional facies between the lower Fayetteville Shale and Pitkin Limestone, consisting of an alternation of limestone and shale lithologies. This limestone-shale rhythmicity represents an important distinctive feature in the field (Handford, 1985). The Ouachita Basin is a Paleozoic remnant marine basin located in the southern-central United States. The tectonic evolution of the Ouachita orogen made a complete Wilson cycle, from the rifting stage (late Cambrian) to ocean basin formation with a passive continental margin (Ordovician), followed by formation of an active margin with a subduction zone (Devonian), and ended with the collisional phase resulting in the formation of the foldbelt and foreland basin (Thomas, 1976, 1977a, b; Golonka et al., 2003). The late Precambrian-early Cambrian rifting developed a continental margin along the southern boundary of North America. Deposition evolved during the rifting from carbonate facies to deepwater clastic sequences. As the Gondwana plate approached the Northern American plate during middle to late Pennsylvanian time, the Ouachita Basin began to close, resulting in the deformation of late Cambrian to carboniferous packages to a foreland fold and thrust belt of the Ouachita Mountains (Zou et al., 2017). The 2000 km of the curved-like belt of the Ouachita extends from the Southern Appalachians to an uncertain and speculative extension in North Mexico where it dies out (Shurbet and Cebull, 1987; Stewart, 1988; Stewart et al., 1993).

The Ordovician to Pennsylvanian Ouachita rocks described as off-shelf deep water sediments consist of, in decreasing abundance, black shales, cherts, novaculite, tuff, limestone, and conglomerate. These deep-water facies covering the largest portion of the Ouachita Mountains constitute the obducted sedimentary sequences tectonically emplaced onto the southern margin

of North America during the Ouachita orogeny (Houseknecht, 1986; Viele and Thomas, 1989). The total thickness of the beds exposed fluctuate between 7 km and 11 km. The low degree metamorphism during the Ouachita Orogeny has moderately affected the rocks, transforming some previous sedimentary units into slate and quartzite.

Shale-dominated rocks deposited in a deep-water basin occupy the pre-Pennsylvanian section. They are ductile, black to gray, clayey to bituminous or siliceous, fissile to blocky, and include the Collier Shale (Upper Cambrian to Lower Ordovician), the Mazarn Shale (Lower Ordovician), the Womble Shale (Middle Ordovician), the Polk Creek Shale (Upper Ordovician), and the Missouri Mountain Shale (Silurian) (Fig. 2). These shales are interbedded with sandstones/quartzite and chert (Crystal Mountain Sandstone, Blakely Sandstone, Bigfork Chert, Blaylock Sandstone, and Arkansas Novaculite) (Keller, 2008). A deep marine arenaceous flysch sequence of the Morrowan Jackfork sandstone consist of an alternation of well sorted medium to fine grained sandstone with shale or silty shale (Cline, 1970; Morris, 1971; Owen and Carozzi, 1986). The Jackfork sedimentological characteristics are indicative of turbidite deposition (Shanmugam and Moiola, 1995; Morris, 1974).

In addition to sedimentary rocks, Cretaceous intrusive igneous rocks are distributed in two small areas in the Ouachita Mountains, one at Potash Sulphur Springs and another at Magnet Cove (Purdue and Miser, Thomas, 1985; Johnson, 1988).

Table 1. Description of rock samples of the study area. Geographic locations of the rocks are provided in Table 2.

Formation	Age	Number of samples	Description of rocks
Jackfork Sandstone (Ouachita Mountains)	Pennsylvanian	8	Thin layers of fine grained and gray sandstone and occasionally interstratification of clayey shale and shaly sandstone beds.
Stanley Shale (Ouachita Mountains)	Mississippian	2	Black, fissile and graphitic slate-like shale due to metamorphism occasioned by increased temperature and pressure during the Ouachita orogeny
Polk creek Shale (Ouachita Mountains)	Late Ordovician	1	Black and graphitic clay shale with traces of quartzite and cherts
Womble Shale (Ouachita Mountains)	Middle Ordovician	1	Black shale with interbedded sandstone and limestone thin layers
Mazarn Shale (Ouachita Mountains)	Early Ordovician	4	Black to gray-black and clayey shale containing small amounts of silty sandstone and limestone.
Collier Shale (Ouachita Mountains)	Cambrian	2	Black to dark gray shales containing some quartz pebbles
Fayetteville Shale (Ozark Plateau)	Mississippian	3	Black to dark-gray carbonaceous and fissile shale interbedded with fine-grained limestone
Chattanooga Shale (Ozark Plateau)	Devonian/Miss.	3	Black, clayey and slightly sandy and fissile shale

3. The Tri-State and Northern Arkansas Mississippi Valley-type Districts

Horizons hosting MVT ores in the Southern Ozark region are of distinct size and located in distinct stratigraphic units, structural and hydrological settings, as well as different geographic positions. The majority of the ores are located in carbonate and minor clastic rocks of passive margin platform (Fig. 3) ranging in age from Cambrian through Pennsylvanian. There is an apparent southward younging of MVT mineralization from central Missouri to northern Arkansas in the Permian (303 ± 17 Ma in the north; 265 ± 20 Ma in the south) (Leach et al., 2001; Bradley and Leach, 2003; Bradley and Shelton, 2012). A common feature of the Northern Arkansas district is the proximal location to normal faults (Fig. 3), which provided brine pathways that rose from deeper Cambrian-Ordovician carbonate aquifers into shallower sequences dominated by limestones. Steeply dipping fractures and faults intersect breccias in karst-like system situated in close vicinity to ores. Hence, breccias provided high porosity and high permeability, important for metal precipitation from incoming mineralizing fluids (McKnight and Fischer, 1970; Wenz et al., 2012). The similarity in geology and mineralogy and the geographic proximity to one another have led Leach et al. (1975) and Viets and Leach (1990) to attest the same mineralizing events for the Northern Arkansas and the Tri-State MVT districts. Six major deposits that make up the Tri-State district, trending southwest-northeast, are hosted largely by cherty limestones of the Mississippian Boone Formation. Mineralization took place atop of the orogenic forebulge and was controlled by the Miami fault. The local hiatus of the low-permeability Ozark confining unit, which is bracketed regionally by the Springfield Plateau aquifer (Boone Formation) and the basement, facilitated the hot mineralizing fluid flow to pervade into the host Boone Formation (Imes and Smith, 1990). The ore mineral association is characterized by abundant sphalerite and galena ($Zn/Pb = 16$) and a lesser amount of chalcopyrite. Gangue minerals consist of dolomite,

jasperoid, and limestone. Mineral and gangue distribution follows a zonation pattern consisting of, from the center to the edge, the dolomite core, sulfide mineralization, a jasperoid alteration zone, and an unaltered and unmineralized limestone. With a production of around 500 M short tons, the Tri-State district is the second world largest occurrence of MVT mineralization (Brockie et al., 1968; Ohle and Gerdermann, 1989). Around 250 small ore bodies comprise the Northern Arkansas district, with the majority (41%) located in the Rush subdistrict, situated in the west-central part of the district (Long et al., 1986). An incomplete production estimated to 24,000 short tons of Zn and 1,500 short tons of Pb metal was yielded from the Northern Arkansas district. The ores are hosted by the Ordovician Cotter Dolomite, Powell Dolomite, and Everton Formation, and the Mississippian Boone Formation and Hindsville Limestone. Brecciation of host rocks induced by faults and folds is followed by dissolution, leading to the development of dissolution-collapse breccias. In order of their abundance, sulfide ores are sphalerite, galena, chalcopyrite, pyrite, and marcasite. Dolomite, calcite, jasperoid, and quartz comprise the main gangue phase (McKnight, 1935; Brockie et al., 1968; McKnight and Fischer, 1970; Hagni, 1976; Wenz et al., 2012).

The geological attributes of the MVT deposits in the Southern Ozark region, taken in the context of a far-field approach (Goldhaber et al., 1995), allow us to relate the mineralization to a tectonically-induced regional south-north hydrothermal flow system. The hydrothermal fluids may have leached metals from rocks of the Ouachita Mountains, Arkoma Basin, and the Ozark Plateau during their migration up to the favorable setting for ore precipitation. However, the ambiguity in the formation of the Ozark MVT deposits is still pending. There are three main genetic models accounting for the precipitation of sulfide ores: a mixing model (Anderson, 1975;

Beales and Jackson, 1966), a reduced sulfur model (Anderson, 1973; Helgeson, 1970, Sverjensky, 1981), and a sulfate reduction model (Anderson, 1983; Barton, 1967; Macqueen and Powell, 1983). In the first model, mixing of two end-member fluids, a metal-rich sulfide poor fluid and a metal-poor sulfide rich fluid, led to precipitation of sulfide minerals. The reduced sulfur model proposes a concomitant transport of ore metals and reduced sulfur dissolved in brine solutions, with precipitation of sulfide minerals resulting from cooling, dilution, and/or decrease in acidity. A joint transport of sulfate and ore metals in solutions up to the highly reducing depositional environment justifies the sulfate reduction model.

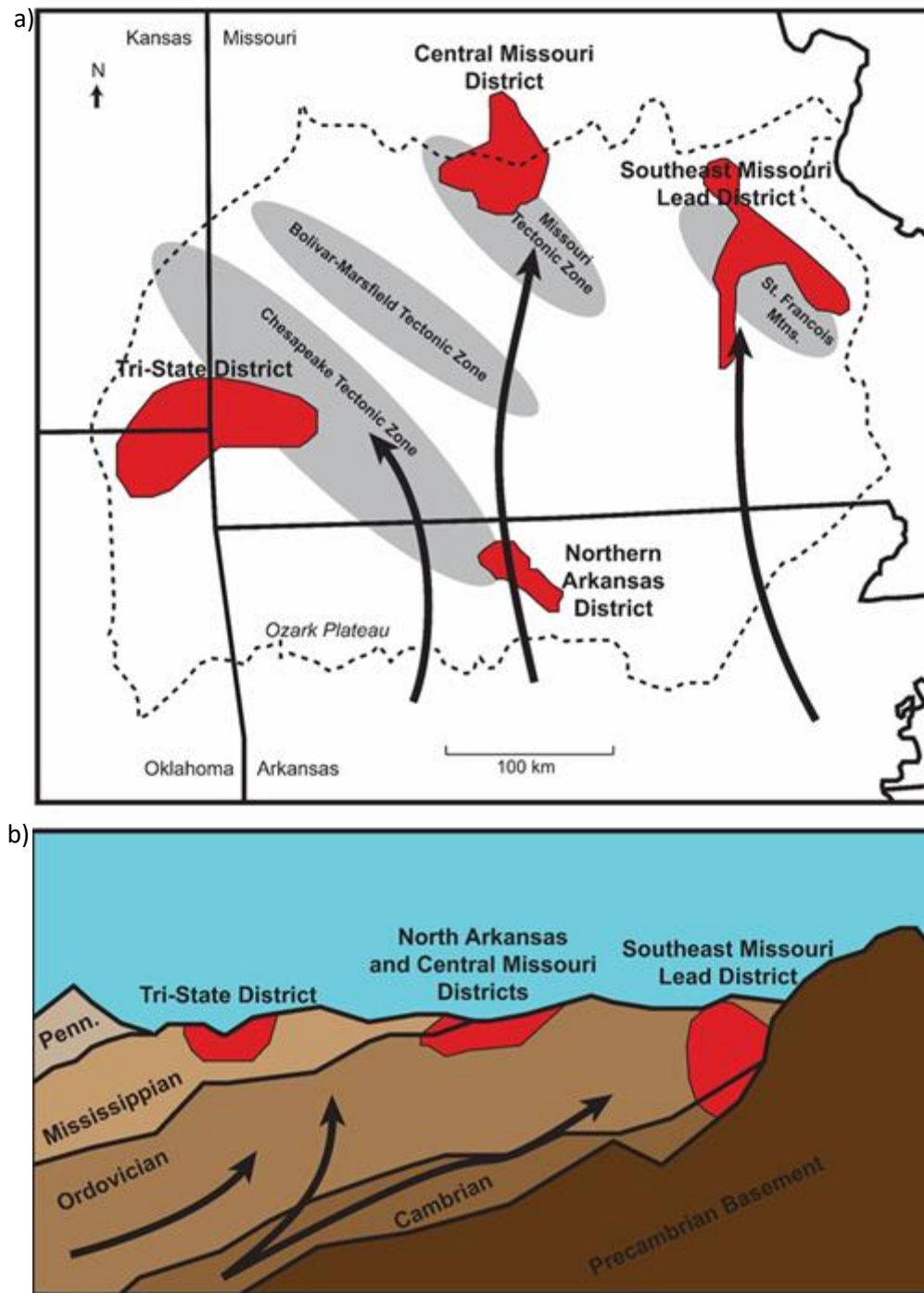


Figure 1. (a) Geologic sketch map showing the location of major MVT ore districts of the Ozark region (b) Cross section showing brine migration (in arrows) during MVT mineralization event (Modified from Lopaka L.,2000).

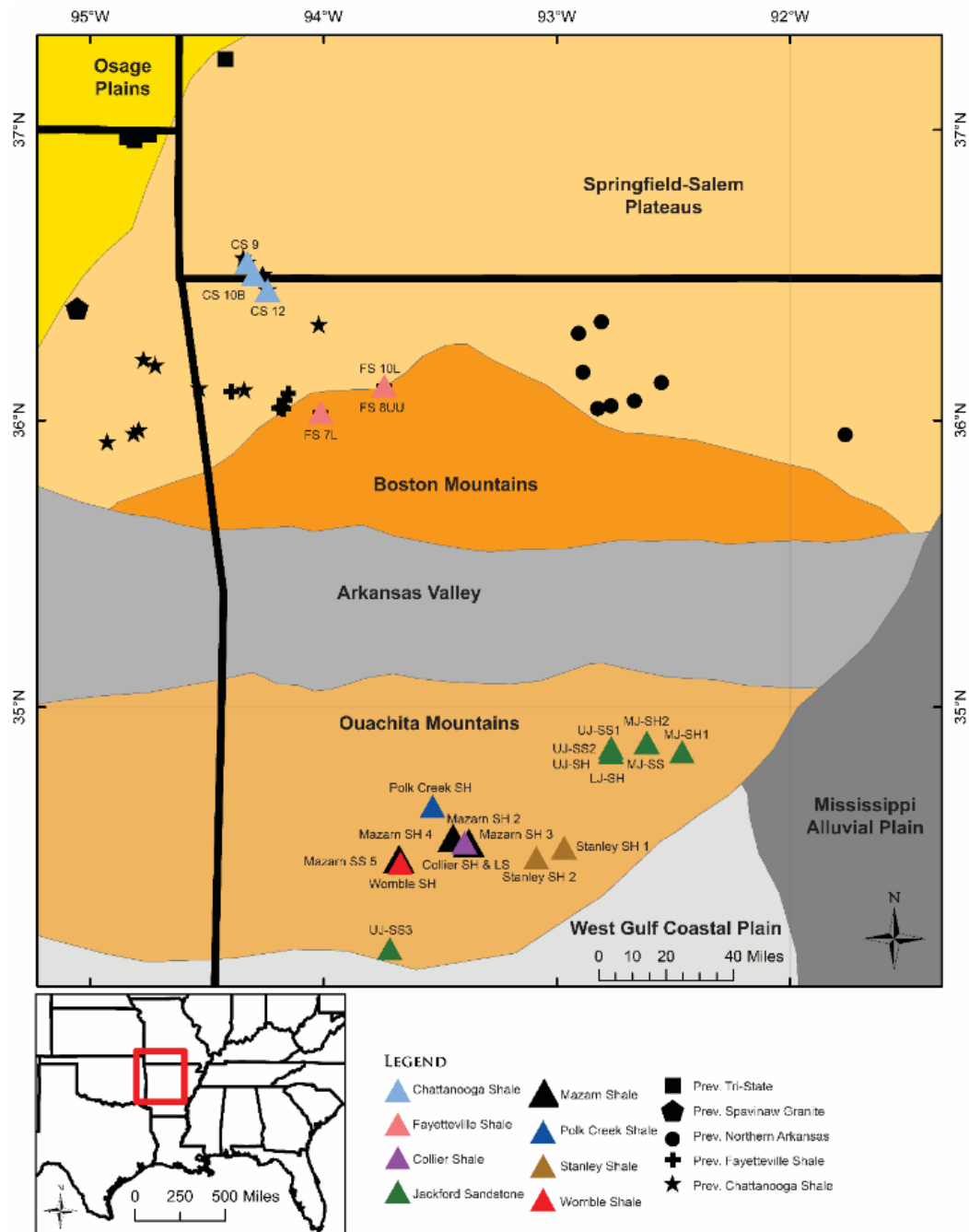


Figure 2. Location of rock samples in the Ouachita Mountains and the Ozark region (the Fayetteville and the Chattanooga shale sample data were taken from Bottoms et al., 2019).

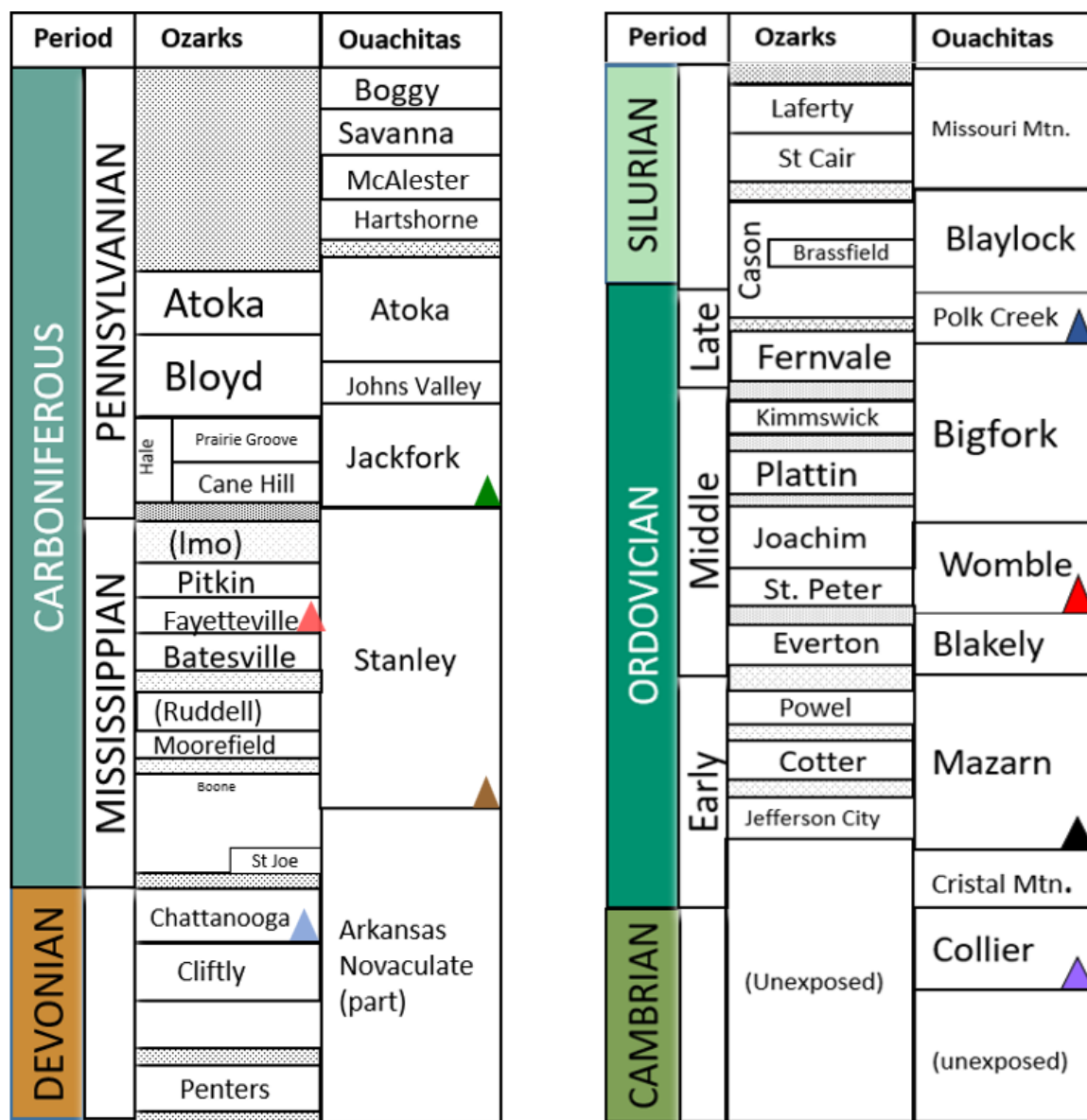


Figure 3. Stratigraphic position of the rock samples in the stratigraphic section of the Ozarks and Ouachitas. Figure 2 gives the location of each rock sample (Retrieved from <http://www.geology.ar.gov/geology/stratigraphy.htm>).

4. Sampling and Analytical Methods

The Paleozoic sedimentary rocks from the Ouachita Mountains analyzed in this study (Fig. 2) were collected in August 2017. Additionally, six shale samples from the Ozark Plateau (Fayetteville Shale and Chattanooga Shale; Table 1), gathered during a previous research project (August 2016), were incorporated in this study. Sampling locations were based on McGilvery and McGee's (2008) field guide that clearly describes all lithologies. Due to the sensitivity of the subsequent geochemical analyses, the sampling had to be carried out with maximum caution to avoid external influence or contamination. Emphasis during sampling was placed on black shales, considered as potential metal source-rocks; however, other rock types were also gathered, in particular sandstones (Table 1). The Ordovician Collier, Mazarn, Womble, and Polk Creek shales, the Mississippian Stanley Shale, and the Pennsylvanian Jackfork Sandstone were sampled. Partial digestion and total digestion experiments were carried out on eighteen shales and sandstones from the above-mentioned lithologies (Table 1). Additionally, partial digestion experiments were conducted on six Fayetteville and the Chattanooga shales (Table 1).

4.1 Sample Processing

The whole-rock sample processing was carried out in the rock room section of the Radiogenic Isotope Class 100 Clean Laboratory at the University of Arkansas. The samples were crushed with a hammer to obtain fresh, unaltered chips of rocks from the crushed rock samples. The selected chips were powdered using a Spex SamplePrep ShatterBox. Between each sample, the alumina ceramic grinding container was cleaned with deionized (DI) water, double distilled (DDI) water, and methanol to avoid cross-contamination. A small amount of pure quartz sand that had been previously acid cleaned in nitric acid was added to the container and powdered in order to aid the cleaning process. The chemical processing of the powdered samples was carried

out in the Radiogenic Isotope Class 100 Clean Laboratory at the University of Arkansas. Total digestion (trace element concentrations and Pb isotope compositions) and partial digestion (Pb isotope compositions) experiments were carried out on the whole-rock samples. The objective of the total digestion stage is to constrain the signature of fluid-rock interaction system during brine migration up to their favorable conditions for depositional setting. Leaching experiments (partial digestion) that mimic the behavior of hydrothermal fluid systems were conducted to assess the potential of hydrothermal fluids to scavenge leachable Pb metals from the rocks. The leaching experiments followed the methods described by Chiaradia and Fontboté (2003). Higher leaching temperature and a longer leaching time, mixing of strong acids HNO_3 -HCl to reduce immobile Pb^{4+} to mobile Pb^{2+} , and the conversion of rocks into powdered samples facilitate extraction of leachable Pb during leaching experiment (Chiaradia and Fontboté, 2003).

4.2 Chemical dissolution and analyses of whole-rock samples for Pb isotope composition

Because Pb occurs at trace levels, the ensuing analytical technique required a pre-concentration step (extraction chromatography) before proceeding to the isotope ratio determination. Following the powdering stage described in section 4.1, 250 mg of powder of each rock sample was weighed and dissolved at 120°C in 2.5ml of HNO_3 , 2.5 ml of HF, and 1 ml of HCl for 12 hours in the muffle furnace. This chemical attack allows complete digestion of the rock samples. The sample solutions were transferred to acid-cleaned Teflon vials and dried down on a hot plate in a class 10 laminar flow hood. One ml of concentrated HNO_3 was added to each sample and heated at 200°C to allow dissolution of the dried sample. Following this step, the lids were removed, and the samples were dried down for the second time. 1.5 ml of 1N HNO_3 was added to each sample and heated again at 200°C to allow dissolution of the sample. The sample solutions were allowed to cool down, transferred to centrifuge tubes, and centrifuged two times for 10

minutes. The solutions were then transferred to acid-cleaned and conditioned columns and the Pb was separated by extraction chromatography (using various acids and Sr-Spec resin purchased from Eichrom), following the column chemistry procedures described by Pin et al. (2014).

Lead isotope analyses were carried out on a Nu Plasma multi-collector ICP-MS located in the Trace Element and Radiogenic Isotope Laboratory at the University of Arkansas using a DSN 100 desolvating system. The samples were diluted with 2% HNO₃ containing 4 ppb Tl prior to analysis. The Pb-Tl mixtures were normalized using the Tl normalization technique for mass bias correction, following the procedure of Kamenov et al. (2004). The data collected for each sample represented averages of 60 ratios per sample. Thirty-nine analyses of the NBS 981 Pb standard carried out during the analyses (February-March 2018) yielded the following results $^{208}\text{Pb}/^{204}\text{Pb} = 36.6804 (\pm 0.0014 \text{ } 2\sigma)$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.4843 (\pm 0.0006 \text{ } 2\sigma)$; $^{206}\text{Pb}/^{204}\text{Pb} = 16.9343 (\pm 0.0006 \text{ } 2\sigma)$. All standard and sample Pb data were normalized to $^{205}\text{Tl}/^{203}\text{Tl} = 2.38750$ and the raw data were corrected using the sample-standard bracketing method and accepted values for the Pb standard from Todt et al. (1996) ($^{208}\text{Pb}/^{204}\text{Pb} = 36.7006$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.4891$; $^{206}\text{Pb}/^{204}\text{Pb} = 16.9956$). Lead blank levels for the water and the acids used in sample processing are uniformly better than 1.2 pg/g. The measured Pb isotope compositions of the analyzed rocks have been age-corrected for in situ U and Th decay to 250 Ma, the age of mineralization (Pan et al., 1990; Brannon et al., 1996). Hence, the stage involving analyses of samples for Pb, U and Th concentrations is critical for the purpose mentioned. The Pb isotope results of whole-rock samples are presented in Table 2 and Table 3.

4.3 Chemical dissolution and analyses of leachates for Pb isotope composition

When rocks are infiltrated by ore fluids, secondary minerals (carbonates, sulfates, oxides) may be abundant. These minerals may introduce exogenous Pb (both, common and radiogenic) after closure of the rock system (Chiaradia and Fontboté, 2003). The differential solubility of primary (silicates and trace sulfides and oxides coeval with rock formation or last recrystallization) and secondary minerals allows separation of Pb introduced into the rock at different times using sequential acid attacks of increasing strength (Chiaradia and Fontboté, 2003). The leachate fraction obtained during a hot HCl - HNO₃ attack contains: (1) bulk Pb (common and radiogenic) associated with soluble primary and secondary minerals, and (2) radiogenic Pb associated with lattice defects of silicate minerals and rock-grain boundaries (Chiaradia and Fontboté, 2003). The Pb isotope composition of the leachate fraction reflects the relative proportions and isotopic compositions of these various Pb sources, while the Pb isotope signature of the residue fraction represents the Pb incorporated by the leach-resistant silicate minerals at rock formation or last recrystallization (Chiaradia and Fontboté, 2003). Therefore, it is important to know the isotopic signature of the leachate portion in order to evaluate the Pb fraction that can be removed by the hydrothermal fluid from the source rock.

For the leaching experiments, 300 mg of powder of each rock sample was weighed and strongly leached at 180°C for 24 hours in 3.5 ml of 7N HCl and 1.5 ml of 14.4 N HNO₃ in screw-sealed Teflon beakers (following the methods described by Chiaradia and Fontboté, 2003). This strong acid attack aims at dissolving common secondary minerals (sulfides, sulfates and carbonates) and scavenging Pb in silicates and intergranular positions, except the leached resistant silicate mineral (zircon) (Chiaradia et al., 2002). The sample solutions were subsequently centrifuged two times for 10 minutes at 180° rotation, resulting in the mechanical separation of

liquid (leachates) and solid (residues) phases. The leachate fractions were carefully extracted and separated from the residues before being dried down and redissolved in 1 mL of 1N HBr for a total of three times. Following these steps, Pb was separated and purified using cation exchange columns and an HBr medium (Manhes et al., 1978). The samples contained in 1N HBr were loaded in columns pre-packed with clean resin (Dowex 1x8-200) and allowed to drain. The Pb was adsorbed on the resin while other elements passed through. Before sample collection, each sample was rinsed in three successive additions of 1 ml 1N HBr. For sample collection, 1 ml of 20% HNO₃ was added to each sample and the sample solutions were dried down. Lead isotope analyses were carried out following the procedures outlined in section 4.2. The Pb isotope results of whole-rock leachates are presented in Table 2.

4.4 Chemical dissolution and analyses of whole-rock samples for trace element concentration

An amount of 250 mg of rock powder was weighed and placed in Parr acid digestion bombs. 2.5 ml HNO₃, 2.5 ml HF, and 1 ml HCl were added to each sample powder. The sample solution was placed in the muffle furnace for 12 hours set at 120°C. This chemical attack allows complete digestion of the rock samples. The sample solution was dried down, and 1 ml of concentrated HNO₃ was added to it. Following this step, the sample solution was placed on the hot plate set at 150° and dried down one more time. A subsequent addition of 2 mL of 7N HNO₃ to the sample was required to redissolve the sample. 0.2 mL of sample was removed and mixed with 4.8 mL of triple distilled water to obtain a sample solution in 2% HNO₃, ready to be analyzed for trace element concentrations on a Thermo Scientific iCAP Q ICP-MS. In order to build calibration curves and constrain the accuracy and reproducibility of the measurements, six USGS rock standards (AG-2, BHVO-2; BIR-1a; DNC-1; QLO-1a; W-2a) were measured along with the

samples. The concentration analyses of redox sensitive trace elements and Pb, U and Th trace elements were done on a Thermo-Scientific ICAP Q ICP MS located in the Trace Element and Radiogenic Isotope Laboratory at the University of Arkansas. The U, Th, and Pb concentrations allow age-correction calculations to be carried out on the whole-rock samples. The redox sensitive trace elements will serve in paleoredox and paleoproductivity studies. The results showing the trace element concentrations are found in Table 5.

5. Metallogenetic study

Lead isotope ratio analyses on whole-rock and leachate samples were performed to trace metal sources and to improve the mineralization model of the Northern Arkansas and the Tri-State MVT districts. Eighteen samples from the Ouachita Mountains (Collier Shale, Mazarn Shale, Womble Shale, Polk Creek Shale, Stanley Shale, Jackfork Sandstone) were analyzed for whole-rock Pb isotope compositions (Table 2; Table 3) and leaching experiments were performed on nine of these samples (Collier Shale, Womble Shale, Jackfork Sandstone) (Table 4). Additionally, leaching experiments were carried out on six samples from the Ozark Plateau (Chattanooga Shale and Fayetteville Shale), previously analyzed by Bottoms et al. (2019) for whole-rock Pb isotope ratios. Previously published Pb isotope data (Potra et al., 2018; Bottoms et al., 2019) of sphalerite ore samples from the Northern Arkansas and the Tri-State MVT mining districts, and of shale samples from the Ozark Plateau (Chattanooga Shale and Fayetteville Shale), have been incorporated in this study (Fig. 2).

The Northern Arkansas and the Tri-State ores are generally more radiogenic than the rock samples and this trend is consistent for both, the measured and the initial Pb isotope composition of whole-rocks (Fig. 4; Fig. 5), as well as for the measured Pb isotope compositions of leachates (Fig. 6). However, one sample collected from the bottom of the Chattanooga Shale shows Pb isotope ratios that plot within the range of those defined by the Northern Arkansas and the Tri-State ores. The ores yield a wide range of Pb isotope ratios (Figs. 4, 5, 6), which are more radiogenic than the average crustal growth curves of Stacey and Kramers (1975) and the orogene growth curve of Zartman and Doe (1981) and correspond to future ages. These anomalous ores enriched in radiogenic isotopes were coined by Nier (1938) as “J-type” ores following the discovery of highly radiogenic galena at Joplin, Missouri. The Pb isotope ratios of this anomalous Pb do not

fit the single-stage model of Pb evolution and correspond to future Pb-Pb ages. The overlap between the isotopic compositions of sphalerites in both districts is indicative of the ores being sourced from a related hydrothermal fluid. The Pb isotope compositions of ores in both districts show a broad and a linear range of isotopic values. This trend suggests mixing of Pb from two distinct end-member components. One end-member must be highly radiogenic, with Pb isotope ratios equal to or higher than the highest noticed value for ores. The other end-member must be less radiogenic, with Pb isotope ratios equal to or lower than the lowest value recorded for ores.

However, in their investigation of the geochemical signatures of Chattanooga and Fayetteville shales in relation to the MVT ores in the Southern Ozark region, Bottoms et al. (2019) concluded that (1) organic-rich shales deposited mainly under nonsulfidic anoxic conditions represent the less radiogenic end-member, or (2) organic-rich shales are the only source of ore metals. In favor of the latter conclusion, they argued that given the array of organic molecules, each with their own thermochemical range, and the ways metals can be associated with them, the release of metals may cover varying ranges. Thus, the compositions of the released fluids would change through time and not have a single static composition, closely approximating the isotopic composition of the released metals at various times. Mineralization derived from a dynamically evolving fluid may show apparent end-members, without the need to call on mixing of fluids from separate sources. Therefore, the linear pattern described by the ores can be attributed to intermittent brine leaching of metals from source rock(s) following progressive crack-down of organic molecules of black shales.

Except for one Chattanooga Shale sample, the age-corrected (250 Ma, the age of the ores) Pb isotope compositions of rock samples (Fig. 6) do not show the highly radiogenic signature displayed by the ores. On the thorogenic diagram (Fig. 6a), several samples from the Jackfork

Sandstone (two samples) and the Chattanooga Shale (one sample) plot to the left of the non-radiogenic end of the ore samples, falling along the non-radiogenic extrapolation of the linear trend defined by the ores. However, the majority of the analyzed samples display a non-radiogenic and a ^{208}Pb -depleted signature compared to the ores (Fig. 6a), and do not fall along the non-radiogenic extension of the linear trend defined by the ores. This trend suggests that the majority of the analyzed samples could not have supplied Pb to the ores. If the upper crust growth curve of Zartman and Doe (1981) was hypothetically extended beyond the 0 Ga value to “future ages”, the ores would lie parallel to this curve, displaying a ^{208}Pb -depleted signature compared to the upper crust curve. A different trend is seen on the uranogenic diagram (Fig. 6b), where the ores would lie above the same growth curve, displaying a ^{207}Pb -enriched signature compared to the upper crust curve (Fig. 6b). From these two Pb isotope diagrams, it appears the best candidates for contributing Pb to the ores are the sandstone members of the upper and middle Jackfork Sandstone and the lowermost section of the Chattanooga Shale. It is worth mentioning that the Pb isotope compositions of previously analyzed Upper Boone tripolitic chert samples (McKim, 2018) partly overlap those of the Northern Arkansas and the Tri-State ores (Fig. 6), suggesting a common source of Pb.

The analyzed leachates have lower $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios than the whole-rock samples (Table 2; Fig. 4; Fig. 5). Most of the analyzed leachates have also lower $^{208}\text{Pb}/^{204}\text{Pb}$, except for the Collier Shale, the Womble Shale, and two of the three analyzed Chattanooga Shale samples, which display leachates enriched in ^{208}Pb compared to their corresponding whole-rock samples (Table 2). Given that the whole-rock Pb isotope compositions plot between the residue and the leachate fractions, it is inferred that the residues are consistently more radiogenic than the

leached fractions. This is due to the fact that shales incorporate a high percentage of clay minerals and most of the common Pb is adsorbed or incorporated into these minerals. The radiogenic signature of the residue fraction reflects the low amount of common Pb left in this fraction after leaching and the high proportion of radiogenic Pb incorporated in old detrital zircons. The deficiency in thorogenic Pb noticed in some residues and conversely, enrichment of thorogenic Pb in the leachate fraction, may be explained by the low Th/U of refractory zircon in the Collier and the Chattanooga shales (Table 4). The Th-depleted and U-enriched signatures shown by the Collier Shale leachate (Fig. 5) supports U fractionation in favor of immobile Th in aqueous solutions, which is typical to MVT basinal mineralizing fluids. However, the opposite trend is noticed in the Womble Shale leachate and in the majority of the Fayetteville Shale and Jackfork Sandstone leachates, which show Th-enriched and U-depleted signatures (Fig. 5).

The less radiogenic nature of the leachate fraction, and conversely the more radiogenic nature of the residue fraction, over their whole-rock samples is more conspicuous for the sandstones of the Jackfork Sandstone. The feldspar-rich rocks are expected to have residual fractions with Pb isotope signature corresponding to the common, less radiogenic Pb incorporated by the rock at its formation. The leachate fraction, representing the Pb extracted with this fraction, should be more radiogenic and represent Pb produced by the in-situ decay of U and Th. One possible explanation for the trend noticed in the Jackfork Sandstone is that the sand grains might have been sourced from granitoid basement rocks, which are enriched in Th and U, and thus the residue fraction would be enriched in Pb produced by in-situ decay of U and Th. Similarly, Dickinson et al. (1983) and Mack (1984) have reported that recycled orogenic and cratonic sands comprise sandstone composition. The fact that some of the Jackfork Sandstone leachates plot on the less radiogenic end of the linear trend defined by the ores (Fig. 5) confirms the likelihood of

the Jackfork Sandstone to be the potential source rock for Pb delivered to the MVT ores in the Ozark Region. The same trend is noticed for Chattanooga Shale leachates, with Pb isotope ratios plotting on the less radiogenic end of the linear trend defined by the ores (Fig. 5).

Table 2. Measured Pb isotope composition of the whole rock samples from the Ouachita Mountains and Arkoma Basin

Formation	Ouachita Mountains Rock Type	ID	Latitude	Longitude	²⁰⁶ Pb / ²⁰⁴ Pb _m	²⁰⁷ Pb / ²⁰⁴ Pb _m	²⁰⁸ Pb / ²⁰⁴ Pb _m
Jackfork Sandstone	Sandstone_1 (Upper)	UJ-SS1	34.8574	-92.7676	19.601	15.714	38.851
Jackfork Sandstone	Sandstone_2 (Upper)	UJ-SS2	34.8574	-92.7676	20.706	15.795	39.645
Jackfork Sandstone	Shale (Upper)	UJ-SH	34.8574	-92.7676	18.982	15.650	39.138
Jackfork Sandstone	Sandstone_3 (Upper)	UJ-SS3	34.1475	-93.7158	19.217	15.665	39.106
Jackfork Sandstone	Shale_1 (Middle)	MJ-SH1	34.8431	-92.4629	19.715	15.696	39.030
Jackfork Sandstone	Shale_2 (Middle)	MJ-SH2	34.8765	-92.6144	18.991	15.657	38.636
Jackfork Sandstone	Sandstone (Middle)	MJ-SS	34.8765	-92.6144	18.809	15.638	38.894
Jackfork Sandstone	Shale (Lower)	LJ-SH	34.8408	-92.7679	18.984	15.651	39.101
Mazarn Shale	Shale	Mazarn SH 2	34.5392	-93.4450	19.571	15.604	38.877
Mazarn Shale	Shale (Upper)	Mazarn SH 4	34.4656	-93.6770	18.787	15.579	39.512
Mazarn Shale	Sandstone	Mazarn SS 5	34.4656	-93.6770	17.815	15.428	37.381
Mazarn Shale	Shale	Mazarn SH 3	34.5219	-93.3773	19.481	15.510	39.074
Stanley Shale	Shale	Stanley SH 1	34.5059	-92.9691	18.960	15.673	39.137
Stanley Shale	Shale	Stanley SH 2	34.4693	-93.0881	19.350	15.677	39.230
Collier Shale	Shale	Collier SH	34.5232	-93.3957	20.014	15.716	38.388
Collier Shale	Limestone	Collier LS	34.5232	-93.3957	16.931	15.767	39.017
Womble Shale	Shale	Womble SH	34.4504	-93.6704	18.736	15.597	38.608
Polk Creek Shale	Shale	Polk Creek SH	34.6513	-93.5328	26.747	16.092	38.525

The subscript m implies measured value.

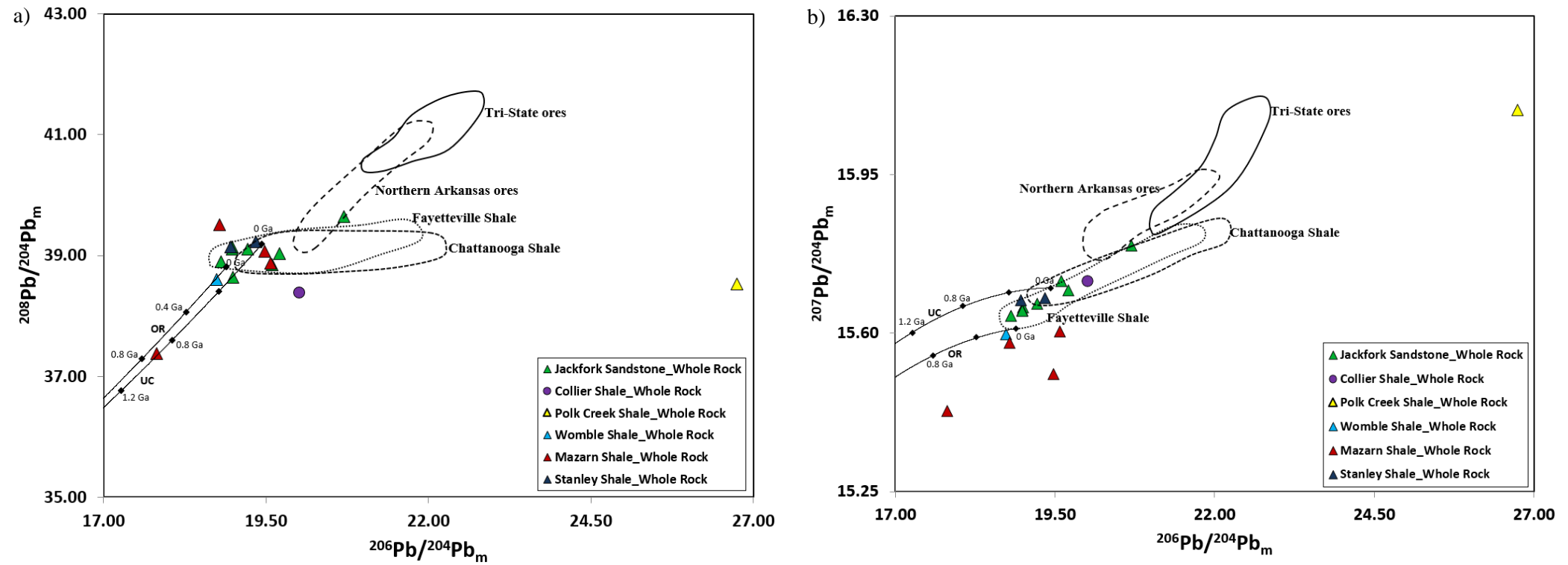


Figure 4. Thorogenic (a) and Uranogenic (b) diagrams depicting the Pb isotope compositions of ores from the Northern Arkansas and the Tri-State MVT districts, and the whole rock samples of the study area. The orogene (OR) and upper crust (UC) growth curves are from Zartman and Doe (1981).

Table 3. Age-corrected (250 Ma) Pb isotope composition of the whole rock samples from the Ouachita Mountains and Arkoma Basin

Formation	Rock Types	ID	²⁰⁶ Pb / ²⁰⁴ Pb _c	²⁰⁷ Pb / ²⁰⁴ Pb _c	²⁰⁸ Pb / ²⁰⁴ Pb _c
Jackfork Sandstone	Sandstone_1 (Upper)	UJ-SS1	18.846	15.587	35.806
Jackfork Sandstone	Sandstone_2 (Upper)	UJ-SS2	19.269	15.721	32.426
Jackfork Sandstone	Shale_1 (Middle)	MJ-SH1	19.400	15.680	36.437
Jackfork Sandstone	Sandstone (Middle)	MJ-SS	18.593	15.627	38.027
Jackfork Sandstone	Shale (Lower)	LJ-SH	18.714	15.637	38.598
Jackfork Sandstone	Shale (Upper)	UJ-SH	18.635	15.633	38.787
Jackfork Sandstone	Sandstone_3 (Upper)	UJ-SS 3	18.747	15.641	38.052
Mazarn Shale	Shale	Mazarn SH 4	18.018	15.540	36.060
Collier Shale	Shale	Collier SH	18.498	15.638	35.698
Collier Shale	Limestone	Collier LS	13.731	15.603	38.878
Womble Shale	Shale	Womble SH	18.347	15.577	36.631
Polk Creek Shale	Shale	Polk Creek SH	23.625	15.933	36.652
Chattanooga Shale*	Shale	CS 9	18.697	15.650	38.250
Chattanooga Shale*	Shale (Lower)	CS 10B	21.489	15.878	40.438
Chattanooga Shale*	Shale	CS 12	18.996	15.666	37.773
Fayetteville Shale*	Shale (Lower)	FS 7L	18.684	15.662	37.130
Fayetteville Shale*	Shale (Upper)	FS 8UU	18.581	15.629	35.302
Fayetteville Shale*	Shale (Lower)	FS 10L	18.552	15.626	38.412

* For location of samples and measured Pb isotope ratios, see Bottoms et al. (2019).
The subscript c implies the corrected value. The concentration16) values used for the age-correction are found in table 5.

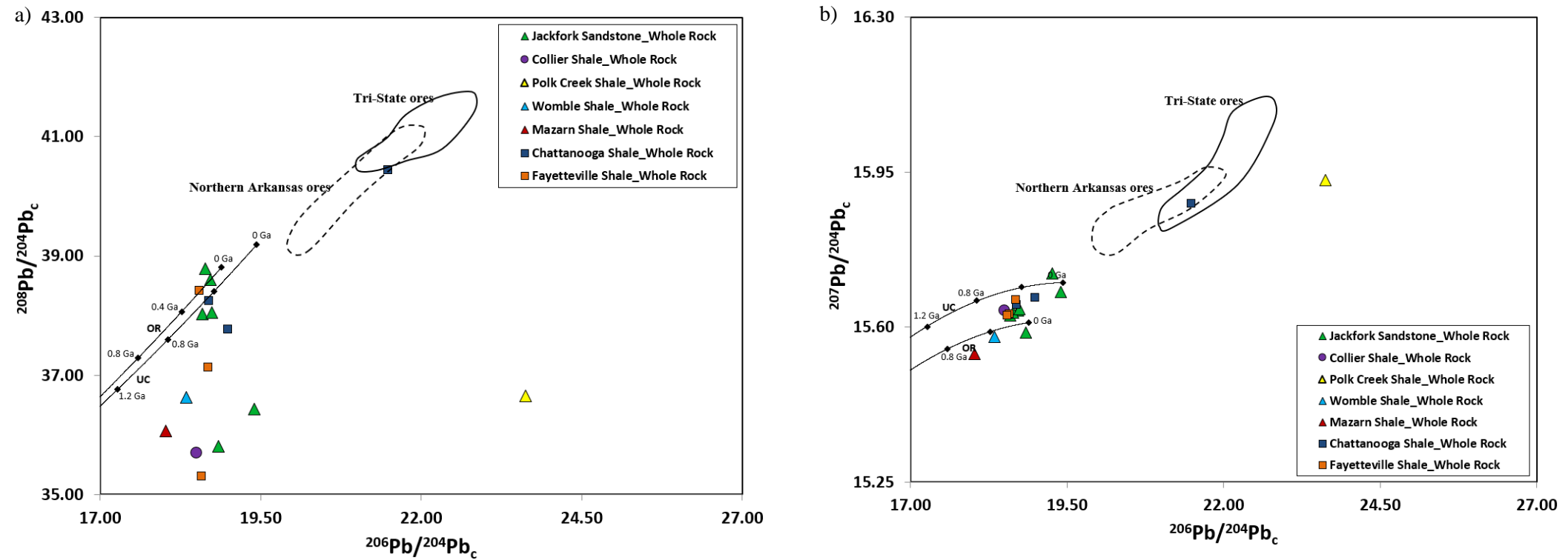


Figure 5. Thorogenic (a) and Uranogenic (b) diagrams depicting the Pb isotope compositions of ores from the Northern Arkansas and the Tri-State MVT districts, along with the age-corrected (250 Ma) Pb isotope values of whole rock samples of the study area.

Table 4. Measured Pb isotope composition of the leachate fraction of rock samples from the Ouachita Mountains and Arkoma Basin

Formation	Rock Type	ID	²⁰⁶ Pb / ²⁰⁴ Pb _m	²⁰⁷ Pb / ²⁰⁴ Pb _m	²⁰⁸ Pb / ²⁰⁴ Pb _m
Jackfork Sandstone	Sandstone_1 (Upper)	UJ-SS 1	18.684	15.626	38.650
Jackfork Sandstone	Sandstone_2 (Upper)	UJ-SS 2	19.189	15.661	38.551
Jackfork Sandstone	Sandstone (Middle)	MJ-SS	18.637	15.627	38.843
Jackfork Sandstone	Shale_1 (Middle)	MJ-SH 1	18.551	15.624	38.551
Jackfork Sandstone	Shale (Upper)	UJ-SH	18.674	15.570	38.822
Jackfork Sandstone	Sandstone_3 (Upper)	UJ-SS 3	18.835	15.629	39.022
Jackfork Sandstone	Shale (Lower)	LJ-SH	18.686	15.622	38.973
Collier Shale	Shale	Collier SH	19.702	15.705	38.395
Womble Shale	Shale	Womble SH	18.479	15.539	38.617
Chattanooga Shale	Shale	CS 9	19.091	15.675	38.813
Chattanooga Shale	Shale (Lower)	CS 10B	21.801	15.894	40.834
Chattanooga Shale	Shale	CS 12	19.453	15.683	38.845
Fayetteville Shale	Shale (Lower)	FS 7L	20.014	15.728	39.347
Fayetteville Shale	Shale (Upper)	FS 8UU	18.709	15.627	38.901
Fayetteville Shale	Shale (Lower)	FS 10L	18.601	15.584	38.758

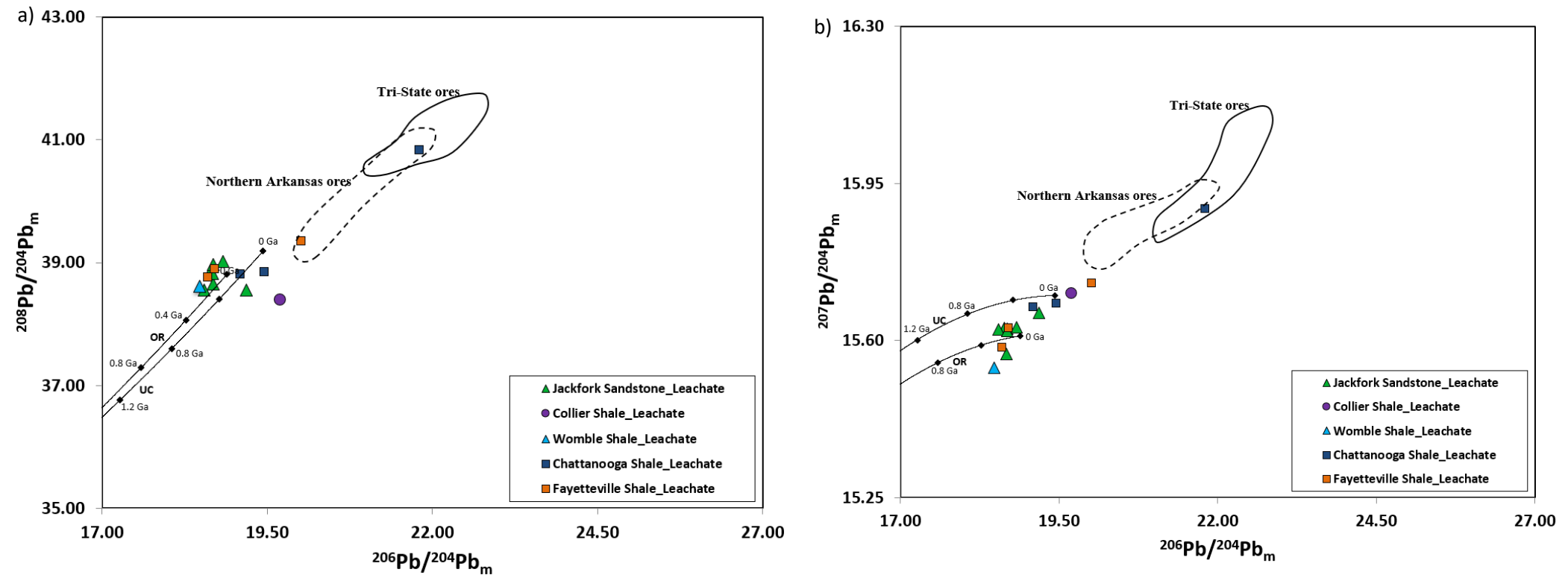


Figure 6. Thorogenic (a) and Uranogenic (b) diagrams showing the Pb isotope compositions of ores from the Northern Arkansas and the Tri-State MVT districts, along with the measured Pb isotope ratios of the leachates.

6. Paleoredox and paleoproductivity investigations of the Study area

6.1. Background and Results

In the previous section, Pb isotope proxies have been used to provide insights into the provenance of metals in the MVT ores from the southern Ozark Region, with the best candidates represented by the Jackfork Sandstone (Ouachita Mountains) and the Chattanooga Shale (Ozark Plateau). The framework of the paleoredox investigation in this study is based on the assumption that black shales are considered sinks for metals, as asserted by Coveney and Glascock (1989). If the sinking function of black shales was effective enough to be able to accomplish a sourcing function for MVT ore metals (Long and Angino, 1982), an incomplete chemical weathering of trace elements (TEs) from potential source rocks must have occurred. The majority of these fine-grained particles are organic carbon-rich sediments that have been geochemical sinks for trace elements and record signals of the dynamic changes of the past marine redox conditions. Therefore, they act as important archival repository of geochemical information, including trace metals (Sageman et al., 2014). The solubility of certain transition elements, known as redox sensitive trace metals, is strongly controlled by redox conditions (Fig. 7), inducing their use as redox proxies in modern and ancient sedimentary systems. Among them, U, V, Mo and, to some extent, Cr and Co are particularly useful as paleoredox proxies, whereas micronutrient elements (Ni, Cu, Zn and Cd) linked to organic matter determine the paleoproductivity of the sedimentary environment (Tribovillard et al., 2006; Algeo and Maynard, 2008). In addition to U, V, and Mo (Emerson and Huested, 1991; Tribovillard et al., 2006), the three most widely used and agreed upon TEs as tracers of paleoredox conditions, Re (Crusius et al., 1996; Morford and Emmerson, 1999), Zn (Algeo and Maynard, 2004), Ni and Pb (Cruse and Lyons, 2004) are also important tracers.

While TEs in shales consist of detrital (transported or particulate), authigenic (precipitated, redox-driven), and biogenic (calcium carbonate and organic matter) components, paleoredox studies are conducted on authigenic TE budgets to unravel their enrichment or depletion, two sedimentary processes controlled by the redox conditions (Sageman and Lyons, 2003).

There are four main redox conditions depending on oxygen concentration in bottom waters. Oxygen availability in sediments is controlled by molecular diffusion and bioturbation or water currents (Huettel and Gust, 1992a) or by the oxidation of organic matter and reduced inorganic metabolites (Jørgensen, 1983) (fig.7 and 8). Oxidation of OM is done following a sequence of electron acceptor from O_2 to Mn^{4+} to NO_3^- to Fe^{3+} , SO_4^{2-} and CO_2 (Fig.8).

Redox classes	Oxic	Suboxic	Anoxic	Euxinic
			No free H_2S in the water column	Free H_2S present in the water column
O_2 concentration in bottom waters (ml O_2 / l H_2O)	Oxic	Suboxic	Anoxic	Euxinic
	$[O_2] > 2$	$2 > [O_2] > 0.2$	$[O_2] < 0.2$	$[O_2] = 0$

Figure 7. Redox classification of depositional environment (adapted from Tyson and Pearson, 1991).

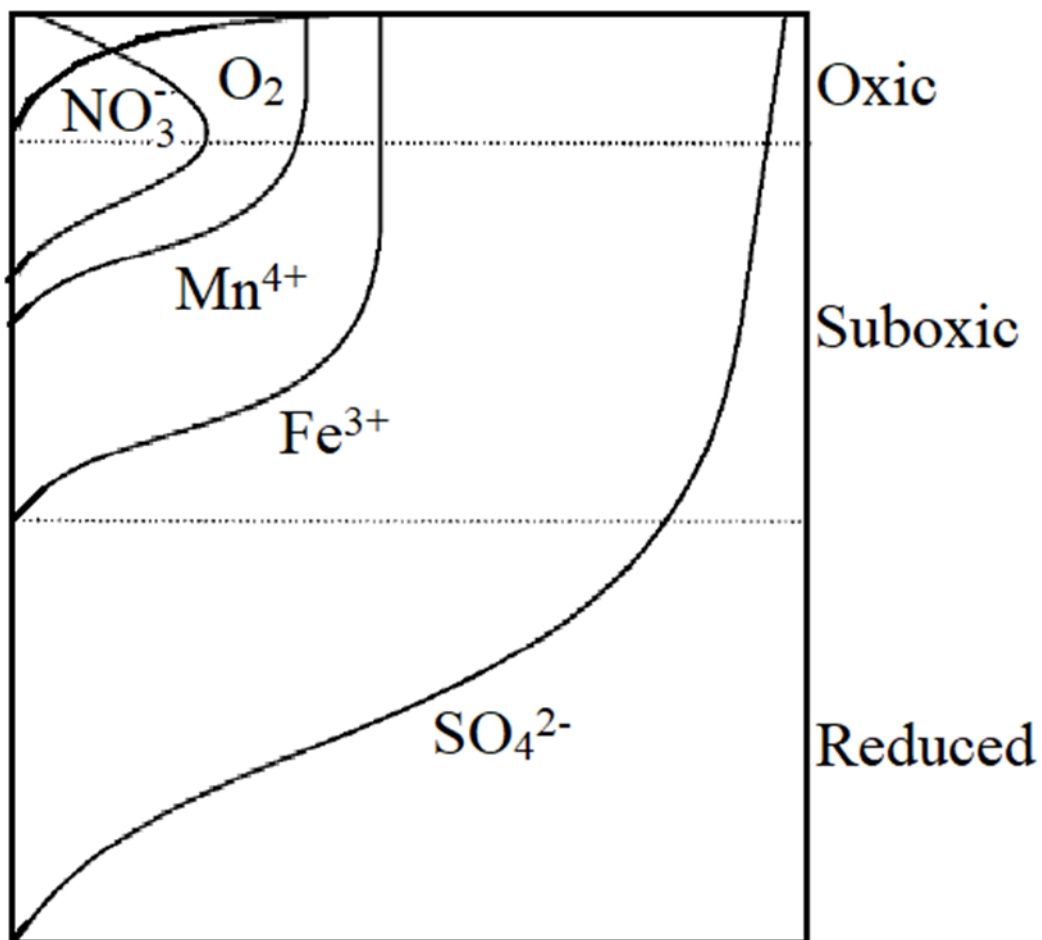


Figure 8. Vertical profiles of electron acceptors in marine sediments (Adapted from Kristensen, 2000).

To isolate the authigenic TE inputs in shales, their concentrations are normalized to a typical detrital element (Al, Ti, Sc, Th) and the obtained values are compared to their corresponding average crustal or shale values considered as cutoff for detrital budgets (Cole et al., 2017). Trace element concentrations of the Post Archean Australian Average Shale (PAAS; Taylor and McLennan, 1985) will be used in this study as an average shale value reference. Spatial and temporal variation in the distribution and concentration of redox sensitive trace elements has led to an inefficient use of a single TE as a paleoredox tracer. Hence, multi-proxy approach is recommended in probing past depositional environment of sediments. It is customary to use enrichment factors (EF) to interpret normalized TE results (Brumsack, 2005; Tribovillard et al., 2006). The EF is defined as:

$$EF_{\text{element X}} = (X/Ti)_{\text{sample}} / (X/Ti)_{\text{average shale}},$$

where X and Ti are trace element and Ti concentrations. $EF_{\text{element X}}$ greater than 1 indicates enrichment of that particular TE relative to PAAS, while depletion is expressed by $EF_{\text{element X}}$ less than 1.

The redox sensitive TEs and their ratios used in this study to reconstruct the paleodepositional and paleoredox conditions of sediments are U, V, Mo, Cr, Co, Cu, Zn, Cd, Th, Ti, and Pb, plus the V/(V+Ni) ratio (Table 5). In addition, the relative enrichment of metals over the average shale values (standards) have been added to constrain the paleoredox conditions, using the EF values (Table 6). Ti was used as a detrital tracer to normalize TE concentrations and constrain the authigenic fraction. Despite potential errors associated with the normalization process, Ti is treated here as a conservative tracer of detrital input (Weijden, 2002). In contrast to the hydrothermal input to the Al budget (Von Damm et al., 1985; Lunel et al., 1990; Elderfield et al.,

1993; Resing et al., 2015), generally used as an indicator of detrital fraction, Murray et al. (1993) favored the use of Ti, arguing to its essential provenance from lithogenic fraction.

Table 5. Concentration in ppm of Trace Elements and the value of the paleoredox proxy V/(V+Ni)

Formation	ID	U	V	Mo	Cr	Co	Ni	Cu	Zn	Cd	Th	Ti	Pb	V/(V+Ni)
Jackfork Sandstone	UJ-SS1	2.18	15.26	0.24	27.83	5.28	14.29	7.08	50.39	0.04	27.04	3972.20	7.42	0.516
Jackfork Sandstone	UJ-SS2	2.96	17.47	0.28	43.79	5.69	13.64	6.09	48.42	0.03	45.79	4119.20	5.44	0.562
Jackfork Sandstone	UJ-SH	4.91	256.77	1.03	199.09	20.72	93.78	28.37	127.74	0.16	15.26	10914.04	36.12	0.732
Jackfork Sandstone	UJ-SS3	4.33	95.74	1.76	95.48	19.93	67.66	33.09	91.26	0.23	29.81	6088.17	23.57	0.586
Jackfork Sandstone	MJ-SS	0.94	22.54	0.80	39.16	6.86	15.63	6.02	63.81	0.07	23.74	4370.12	7.68	0.591
Jackfork Sandstone	MJ-SH1	2.29	67.45	0.61	64.40	16.17	53.97	22.72	75.35	0.05	28.22	4792.36	26.91	0.556
Jackfork Sandstone	LJ-SH	2.65	155.00	0.97	126.31	18.34	55.78	38.00	70.01	0.14	15.18	7877.48	25.05	0.735
Mazarn Shale	Mazarn SH 4	3.63	129.69	0.28	68.06	12.77	41.43	24.44	91.47	0.08	50.06	5849.38	12.07	0.758
Collier Shale	Collier SH	11.19	137.72	7.99	29.22	6.53	28.92	39.75	63.58	1.88	61.05	4120.90	18.95	0.826
Collier Shale	Collier LS	0.75	15.54	0.26	8.63	4.82	10.34	5.91	47.55	0.05	0.10	3898.52	0.58	0.600
Womble Shale	Womble SH	3.21	127.93	2.61	94.62	5.30	35.54	20.57	73.88	0.09	50.14	6094.83	20.85	0.783
Polkcreek Shale	Polk Creek SH	15.44	283.13	33.76	21.70	4.63	23.74	21.66	46.51	0.04	28.50	4064.47	13.91	0.923
Fayetteville Shale	FS 7L	5.10	82.49	6.47	225.17	5.83	55.64	32.63	70.98	0.31	19.99	4207.73	7.27	0.597
Fayetteville Shale	FS 8UU	2.77	64.00	0.48	67.72	11.40	37.88	15.87	614.57	1.64	74.31	5820.74	17.11	0.628
Fayetteville Shale	FS 10L	3.47	241.10	1.18	247.18	26.25	84.70	28.89	132.97	0.24	27.98	9589.04	45.29	0.740
Chattanooga Shale	CS 9	12.63	181.12	28.93	115.48	31.19	99.67	60.23	91.93	0.23	42.80	7532.54	64.47	0.645
Chattanooga Shale	CS 10B	8.47	77.85	35.57	50.56	16.08	52.13	50.80	54.29	0.07	25.18	4471.54	59.36	0.599
Chattanooga Shale	CS 12	11.37	249.13	24.22	122.78	25.80	90.11	71.49	106.70	0.44	69.29	7959.67	42.96	0.734

Table 6. Values of the Enrichment Factor of Trace Elements used for the paleoredox and paleoproductivity study.

Formation	ID	U	V	Mo	Cr	Co	Ni	Cu	Zn	Cd	Th	Pb
Jackfork Sandstone	UJ-SS1	1.175	0.215	0.245	0.494	0.470	0.490	0.428	1.072	0.001	3.817	0.659
Jackfork Sandstone	UJ-SS2	1.542	0.238	0.271	0.750	0.487	0.451	0.355	0.993	0.001	6.233	0.466
Jackfork Sandstone	UJ-SH	0.964	1.319	0.376	1.288	0.670	1.172	0.624	0.989	0.001	0.784	1.168
Jackfork Sandstone	UJ-SS3	1.523	0.882	1.157	1.107	1.156	1.515	1.304	1.267	0.003	2.745	1.366
Jackfork Sandstone	MJ-SH1	1.023	0.789	0.505	0.948	1.191	1.536	1.138	1.329	0.001	3.301	1.982
Jackfork Sandstone	MJ-SS	0.460	0.289	0.728	0.632	0.554	0.488	0.330	1.234	0.001	3.046	0.620
Jackfork Sandstone	LJ-SH	0.720	1.103	0.494	1.132	0.822	0.966	1.158	0.751	0.001	1.080	1.122
Mazarn Shale	Mazarn SH 4	1.329	1.243	0.194	0.821	0.771	0.966	1.003	1.321	0.001	4.798	0.728
Collier Shale	Collier SH	5.819	1.874	7.751	0.501	0.559	0.957	2.315	1.304	0.039	8.307	1.623
Collier Shale	Collier LS	0.412	0.224	0.270	0.156	0.437	0.362	0.364	1.031	0.001	0.014	0.053
Womble Shale	Womble SH	1.129	1.177	1.716	1.096	0.307	0.795	0.810	1.024	0.001	4.613	1.207
Polk Creek Shale	Polk Creek SH	8.140	3.906	33.228	0.377	0.402	0.796	1.279	0.967	0.001	3.932	1.208
Fayetteville Shale_7	FS 7L	2.599	1.099	6.154	3.777	0.489	1.803	1.861	1.426	0.006	2.664	0.609
Fayetteville Shale_8	FS 8UU	1.018	0.617	0.329	0.821	0.691	0.887	0.655	8.922	0.024	7.159	1.030
Fayetteville Shale_10	FS 10L	0.776	1.410	0.491	1.820	0.966	1.205	0.723	1.172	0.002	1.636	1.667
Chattanooga Shale_9	CS 9	3.591	1.348	15.361	1.082	1.460	1.804	1.919	1.031	0.002	3.186	3.021
Chattanooga Shale_10B	CS 10B	4.057	0.976	31.818	0.798	1.269	1.590	2.727	1.026	0.001	3.157	4.685
Chattanooga Shale_12	CS 12	3.466	1.622	12.778	1.076	1.236	1.709	2.438	1.204	0.004	4.969	2.342

6.2. Interpretation

To assess the authigenic component of TEs, i.e. the degree to which the TEs in the Paleozoic sediments have been derived from seawater, which is very important in paleoredox interpretation, the TE concentrations have been correlated with the Ti concentrations (Fig. 8). Correlation of TEs with Ti ranges from moderate to low, in the following order Ni ($R^2=0.6736$) > Co ($R^2=0.5992$) > Cr ($R^2=0.5324$) > V ($R^2=0.4643$) > Pb ($R^2=0.3344$) > Cu ($R^2=0.1775$) > Zn ($R^2=0.0306$) > Mo ($R^2=0.0039$) > Cd ($R^2=0.0034$) > U ($R^2=0.0016$) > Th ($R^2=0.0003$) (Fig.8). Low values of metal versus Ti signal insignificant detrital fraction and hence give great confidence on the results for paleoredox interpretations. Therefore, Zn, Mo, Cd, U, and Th are considered as yielding higher authigenic inputs in accordance with the redox conditions. Mo is regarded by many workers as the most powerful paleoredox tracer in sulfide-rich sediment or water column (Helz et al., 1996; Yarincik et al., 2000; Adelson et al., 2001; Werne et al., 2002; Lyons et al., 2003).

Enrichment and depletion of TEs in sediments demonstrate their variable behavior towards redox conditions. Ni, Co, Cu Zn Cd and Mo are mainly reduced and accumulated in sulfate reducing conditions while Cr, U and V tend to concentrate under denitrifying conditions. This contrasting geochemical behavior can be used to distinguish redox facies in some sedimentary rocks. Using the EF of redox sensitive TEs, it is possible to discriminate redox conditions of sedimentary systems (Tribovillard et al., 2006). Enrichment of U and V correlated with Mo depletion, as in the case of the Upper Mazarn Shale (Table 6; Fig. 9), suggests suboxic/anoxic conditions, without free H_2S in the depositional environment. Besides, coeval enrichment of U, V and Mo indicates euxinic conditions at sediment-water interface or in the water column (Algeo and Maynard, 2004; Tribovillard et al., 2004b, 2005), as observed in Polk Creek Shale, Womble

Shale, and Collier Shale samples (Table 6; Fig. 9). However, other samples (Jackfork Sandstone, Collier Shale, Fayetteville Shale and Chattanooga Shale) do not strictly follow the outlined patterns of EFs of TEs to decipher the redox conditions of their depositional environment. For that reason, they might have been deposited in oxic-suboxic conditions, evidencing a possible high flux of organic matter, the primary production being the first order control of organic-rich sediments deposited in oxic conditions (Petersen and Calvert, 1990) (Table 6; Fig. 9). Tribovillard et al. (2006) agreed upon the oversimplification of the aforementioned criteria of EFs in geological settings with intricate sedimentological factors, which is the case in our study area.

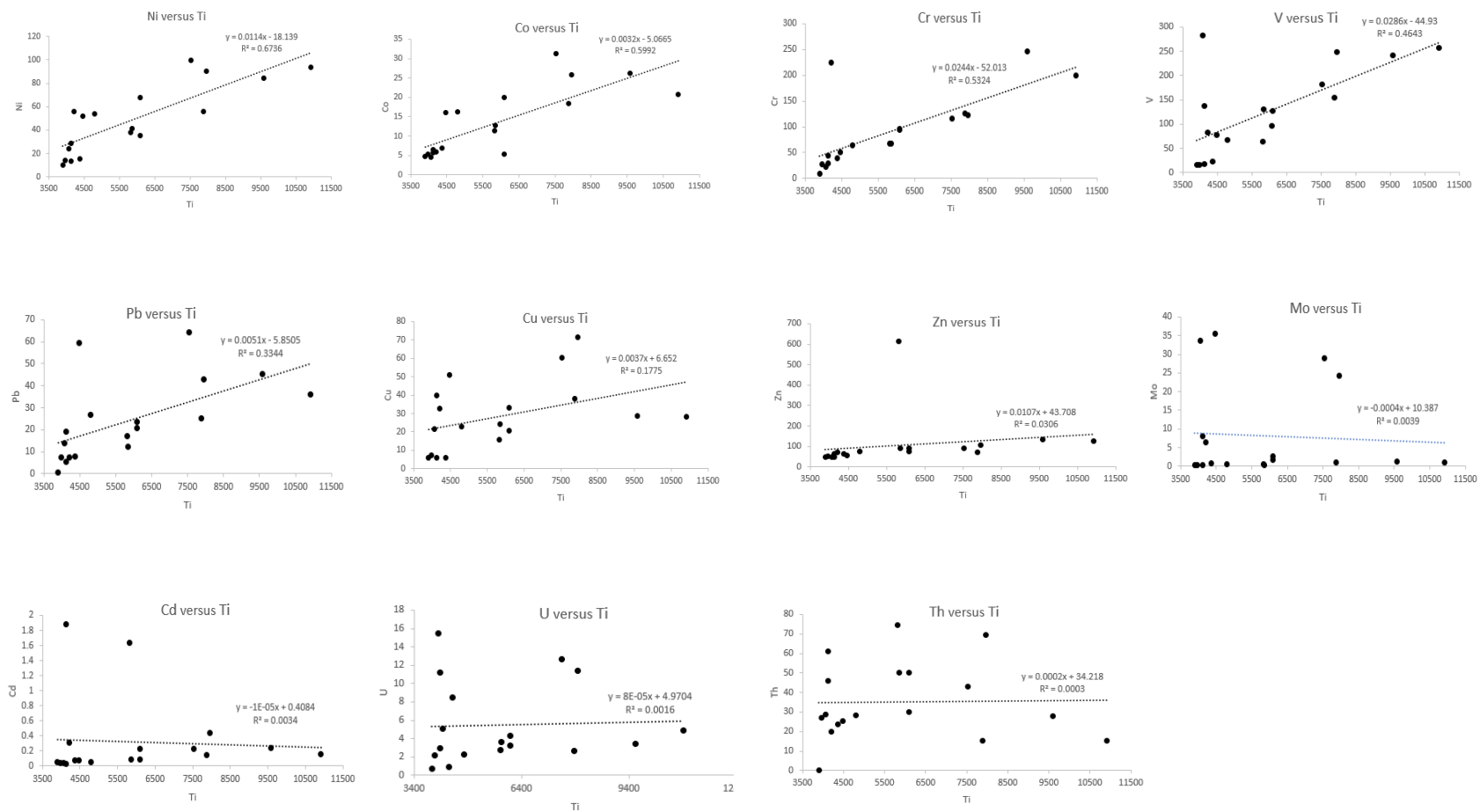


Figure 9. Correlations of various redox-sensitive TEs with the detrital TE Ti. The lower the coefficient of determination (R^2) between a TE and Ti, the higher its authigenic input. In decreasing order of authigenic input, the TE are Th, U, Cd, Mo, Zn, Cu, Pb, V, Cr, Co, and Ni.

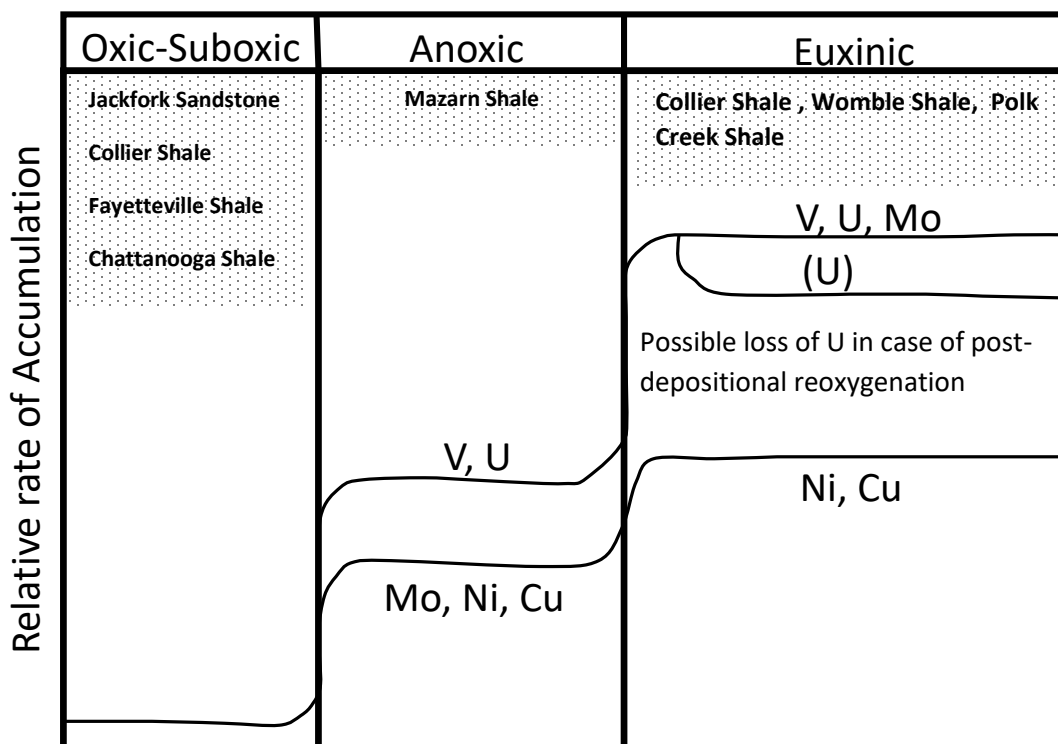


Figure 10. Constraints on the paleoredox conditions during deposition of the rock samples from the Ouachita Mountains and the Arkoma Basin based on Ni, Cu, Mo, U and V behavior (adapted from Tribovillard et al., 2006).

Southerland (2000) defined five categories of enrichment levels: weakly enriched ($1 < EF < 2$), moderately enriched ($2 < EF < 5$), significantly enriched ($5 < EF < 20$), highly enriched ($20 < EF < 40$), and extremely enriched ($EF > 40$). The Mo trend ranges from weakly to highly enriched, depending on the rock sample. The highest enrichment of Mo (Chattanooga Shale and Polk Creek Shale; Table 6) corroborates conclusions made by Crusius et al. (1996), who attributed significant Mo enrichment factor to reducing conditions. In comparison to other redox sensitive trace elements (Cu, Cr, Ni, V, Cd, U), which are enriched in sediments in association with organic matter or precipitate as sulfides or co-precipitate with Fe-sulfides, Tribovillard et al.

(2004) have shown that Mo trapping in sediments is strongly dictated by sulfurized organic material and thereafter diagenesis does not considerably remobilize Mo retention within sediments. Chattanooga Shale and Polk Creek Shale samples might have been enriched in Mo (Table 6) through organic matter sulfurization. Despite limited knowledge of the geochemical characterization of organic materials in sediments in our study area, especially for their organic sulfur content, enrichment in Ni and Co noticed in several samples (Chattanooga Shale and Jackfork Sandstone) (Table 6) reflects abundance of organic matter. Concurrent enrichment in paleoredox and paleoproductivity trace element proxies noticed in the Chattanooga Shale and in the upper and middle members of the Jackfork Sandstone may suggest deposition under oxic conditions associated with high accumulation of organic matter that have complexed with Cu, Ni, Pb and Zn (Petersen and Calvert, 1990). This still substantiates the metallogenetic study of the Northern Arkansas and Tri-State MVT that identified the Chattanooga Shale and the Jackfork Sandstone as potential sources of Pb and or Zn metals. Nevertheless, it has been shown that initial sedimentary record can be overprinted by post-depositional processes, such as burial diagenesis and thermal maturation in black shales, which are alleged to remobilize redox sensitive trace elements (Lev et al., 2000; Algeo and Maynard, 2004).

Because of the spatial and temporal variation of TEs and the fact that no single proxy can significantly define paleoredox conditions, authors agreed on a multi-proxy approach in paleoredox investigations (McManus et al., 2005; Tribovillard et al., 2006; Scott and Lyons, 2012). The $V/(V+Ni)$ ratio is usually used to reconstruct paleoredox conditions, along with V/Cr , Ni/Co , and other ratios (Hatch and Leventhal, 1992; Jones and Manning, 1994; Rimmer et al., 2004). Lewan and Maynard (1982). Lewan (1984) first documented the control of the redox conditions on the $V/(V+Ni)$ ratio in petroleum source rocks and oils. Hatch and Leventhal (1992) further applied

$V/(V+Ni)$ ratios and the degree of pyritization as paleoredox proxies on whole-rock V and Ni analyses of Middle to Pennsylvanian shales. According to these authors, $V/(V+Ni)$ ratios equal to or greater than 0.84 indicate euxinic environment in a strongly stratified water column, while the same ratios ranging from 0.54 to 0.82 and from 0.46 to 0.60 are indicative of anoxic and dysoxic conditions. The $V/(V+Ni)$ ratios obtained in this study (Table 5; Fig. 10) indicate that most samples were deposited in anoxic to euxinic conditions.

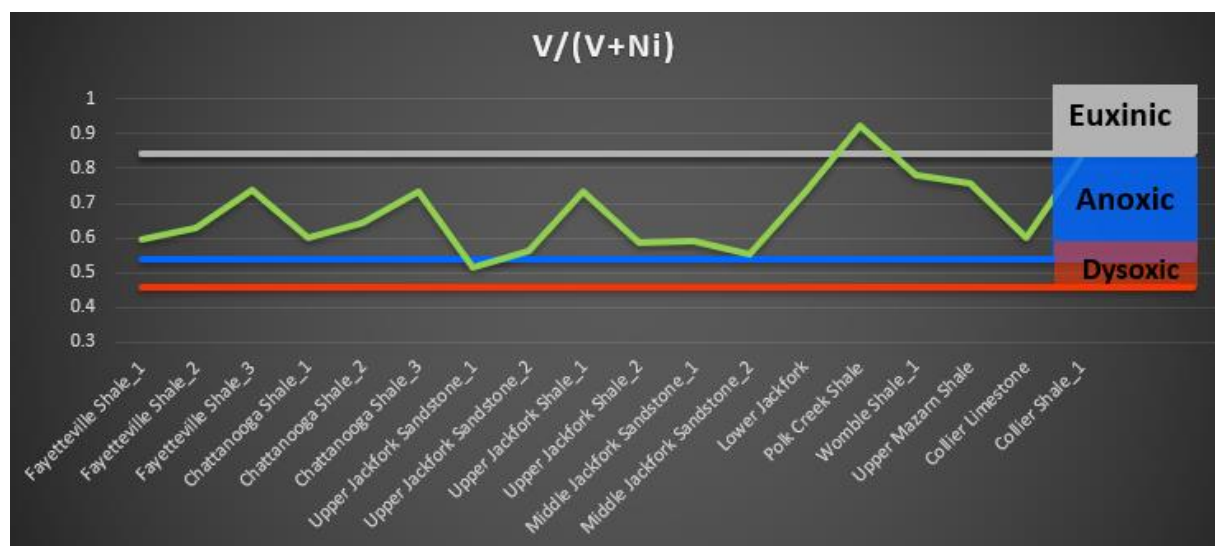


Figure 11. Reconstruction of the paleoredox conditions during deposition of the sedimentary rock samples in the study area using the $V/(V+Ni)$ ratio. According to this geochemical proxy, most of the rock samples were deposited during anoxic conditions.

Studying the hyper-enrichment of V and Zn in black shales of the Late Devonian to Early Mississippian Bakken Formation, Scott et al. (2017) linked the fertility of the Bakken Formation, and by inference the metal-rich black shales in the Paleozoic of North America, to a shallow water depth in the basin. This resulted in a short transit time of organic matter through the water column and led to the occurrence of euxinic conditions.

As noticed, there is generally a disagreement in the redox conditions yielded by the geochemical proxies: the EF of sensitive TE (Fig. 9) and the V/V+Ni ratios (Fig.10). The exceptions are represented by the Polk Creek Shale (deposited under euxinic conditions) and the Mazarn Shale (deposited under anoxic conditions), which show consistent redox conditions for both proxies. This inconsistent observation is common in many paleoredox studies, prompting some authors to raise awareness on using TE ratios in paleoredox investigations. According to some authors, conflicting results may be associated with several factors, including redox potential, pH, sulfur abundance, chemical availability, TOC values, and sediment provenance (Rimmer, 2004; Rimmer et al., 2004; Algeo and Maynard, 2008; Algeo and Rowe, 2012; Xu et al., 2012). Piper and Calvert (2009) pointed out the inaccurate use of TE ratios in bulk sediments, considering the presence of authigenic, biogenic, and siliciclastic components in these sediments and given the fact that the authigenic flux is the only fraction needed to unravel past redox conditions. Rimmer (2003) questioned the thresholds established for TE ratios used as paleoredox proxies of rocks, while they were deposited in different temporal and spatial settings. Additional factors such as the rates of sediment accumulation, the post depositional alteration processes associated with diagenesis and low-grade metamorphism during the Ouachita Orogeny, might have overprinted the depositional signatures.

7. Conclusions and future directions

Metal provenance studies indicate that the sandstone members of the upper and middle Jackfork Sandstone and the lowermost section of the Chattanooga Shale are the possible major sources of Pb, and by inference other MVT metals with similar geochemical behavior (e.g., Zn, Cd, Ga, Ge), in the Northern Arkansas and the Tri-State MVT ores. The Pb isotope trend of these ores suggests mixing of Pb from two distinct end-member components, and the Jackfork Sandstone and the Chattanooga Shale appear to be the best candidates for contributing the less radiogenic Pb. The Pb isotope ratios of the Fayetteville Shale leachate fractions also reveal their potential to provide metals to the Northern Arkansas MVT ores. It thus appears that continual brine leaching of the alleged source rocks might have resulted in metal release, which were further mobilized and precipitated as ores. Of particular interest is to identify the source rock that contributed the more radiogenic component of Pb to the MVT ores. Future petrographic studies of sulfide ore paragenesis, combined with a more detailed sampling of the geological formations in the Ouachita Mountains, the Arkoma Basin, and the Ozark Plateau, will help identify this component. Also, ongoing studies on rocks from the Ozark Plateau look promising in pinpointing this radiogenic end-member.

The paleoredox and paleoproductivity studies reveal the fertile conditions during which rock samples were deposited. While anoxic and euxinic conditions were conducive to metal enrichment during deposition of some of the analyzed samples (Mazarn Shale, Collier Shale, Womble Shale, Polk Creek Shale, and Chattanooga Shale), high organic carbon productivity might also have played a key role in metal content during deposition in oxic-suboxic environment of other rock samples (Jackfork Sandstone, Collier Shale, Fayetteville Shale, and Chatta-

nooga Shale). The fact that specific horizons of the Chattanooga Shale and the Jackfork Sandstone are the best candidates to source economic concentrations of metals implies additional factors that might have favored their enrichment. These factors include initial chemical compositions and other subsequent factors during mineralization: pH, redox potential, sulfur abundance, chemical availability, TOC values, and sediment provenance. However, post depositional factors overprinting initial depositional signatures of rock samples would also have impeded insights on the paleoredox conditions. Tribovillard et al. (2006) also suggested careful consideration when using enrichment factors of trace elements in geological settings with intricate sedimentological factors, which is the case in our study area.

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